The Reaction of Triphenylmethyl Bromide with Potassium O-Ethyl Dithiocarbonate (Potassium Xanthate) in Benzene and Cumene. A Note of Caution on the Application of the Radical Trap Dicyclohexylphosphine as a Probe for Electron-transfer-initiated Reactions of Triphenylmethyl Halides[†]

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The title reaction was studied under conditions where homolysis of the triphenylmethyl-to-sulphur bond of the dithiocarbonate 1d, its main product does not take place, or is negligible. Triphenylmethane 1c, triphenylmethanol 1g and benzophenone were obtained as further products under argon in cumene and in the presence of oxygen in benzene, respectively. This, together with ESR studies, indicates that part of the dithiocarbonate 1d results from single-electron transfer from *O*-ethyl dithiocarbonate anion to triphenylmethyl bromide 1a and out-of-cage recombination of triphenylmethyl and xanthyl radicals **6a**. The main pathways leading to dithiocarbonate 1d appear, under the conditions studied, to be either a polar pathway consisting of two successive S_N2' -type steps [mechanism 2, Scheme 3] and/or an $S_{\rm ET}$ -type reaction [mechanism 3, Scheme 3] with rapid in-cage recombination of triphenylmethyl and xanthyl radicals **6a**. The hydrogen-atom donor dicyclohexylphosphine (DCPH) may not be used for trapping of the triphenylmethyl radicals formed in the title reaction because DCPH acts as a single-electron donor towards bromide 1a, *i.e.* it itself generates triphenylmethyl radicals from the bromide.

Triphenylmethyl bromide 1a and chloride are known to react with nucleophiles, depending on the conditions, either via polar (one or the other variant of the S_N mechanisms) or via radical mechanisms [single-electron-transfer (SET)-initiated reactions], or, competitively, via both. Among the various nucleophiles the reactions of anionic O-nucleophiles have been studied the most extensively.² In contrast, reactions of S-nucleophiles with triphenylmethyl halides have, to our knowledge, been little investigated.3,4 In one of these studies³ a series of S-nucleophiles including lithium propane-2thiolate, butane-1-thiolate and benzenethiolate were allowed to react with triphenylmethyl bromide 1a and chloride in tetrahydrofuran (THF) at room temperature, and ipso 1b and tele substitution products 2a were obtained, in addition to the reductive dehalogenation product 1c, the dimeric product 3, and the disulphide corresponding to the thiolate used. On the basis of a study of the influence of added substances [including dicyclohexylphosphine (DCPH), t-butyl alcohol and p-dinitrobenzene (p-DNB)] and of light on the product distribution as well as of ESR spectroscopic studies the authors suggested that all these products result from SET-initiated sequences, the tele substitution products 2a being the result of in-cage recombination of the two components of triphenylmethyl and thiyl radical pairs but the ipso substitution products 1b resulting from chance encounters of the same radicals after their escape from the solvent cage. Recombination of two identical radicals leads to the dimeric product 3 (via re-aromatization of the intermediate semibenzene 4) and the disulphides, respectively, while hydrogen abstraction by triphenylmethyl radicals from the solvent results in the formation of the reductive dehalogenation product 1c (Scheme 1). The polar mechanism for the formation of the semibenzene-type intermediate 5 of the tele substitution product 2a, viz. direct nucleophilic attack of the thiolate at one of the *para* carbon atoms of the triphenylmethyl

Ph ₃ CX	4-RSC ₆ H ₄ CHPh ₂
1	2
$\mathbf{a}, \mathbf{X} = \mathbf{B}\mathbf{r}$	$\mathbf{a}, \mathbf{R} = \mathbf{Pr}^{i}, \mathbf{Bu}^{n}, \mathbf{Ph}$
$\mathbf{b}, \mathbf{X} = \mathbf{SPr^{i}}, \mathbf{SBu^{n}}, \mathbf{SPh}$	b , $\mathbf{R} = \text{EtOC}(=\mathbf{S})$
$\mathbf{c}, \mathbf{X} = \mathbf{H}$	
$\mathbf{d}, \mathbf{X} = \mathbf{SC}(=\mathbf{S})\mathbf{OEt}$	$4-(Ph_3C)C_6H_4CHPh_2$
$\mathbf{e}, \mathbf{X} = \mathbf{OEt}$	3
$\mathbf{f}, \mathbf{X} = \mathbf{SEt}$	_
$\mathbf{g}, \mathbf{X} = \mathbf{OH}$	
h, X = SC(=O)SEt	

halide $(S_N 2'$ reaction), has, however, not been ruled out with complete certainty.

We report on the reaction of triphenylmethyl bromide **1a** with potassium *O*-ethyl dithiocarbonate (potassium xanthate).

Results and Discussion

Factors affecting the Stability of O-Ethyl S-Triphenylmethyl Dithiocarbonate 1d.—In the course of preliminary studies we have noticed that compound 1d, the main product of the title reaction, gradually decomposes (darkens and partly deliquesces) when kept in a desiccator in ordinary laboratory light. Moreover, solutions of compound 1d gradually turn cloudy in ordinary laboratory light in the presence of air and, after some time, a precipitate of bis(triphenylmethyl) peroxide is formed. Our first task was, therefore, to establish, with the aid of ESR

⁺ Single-Electron-Transfer-Initiated Thermal Reactions of Arylmethyl Halides, Part 15; for Part 14, see ref. 1.

[‡] For a comment on the reliability of DCPH as a probe for the detection of triphenylmethyl radicals generated by single-electron donors from triphenylmethyl halides, see below.

Table 1	. Decomposition	of solutions of	O-ethyl	S-triphenyl	methyl dit	hiocarbonate	1d under	various	conditions
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	Solvent	Conditions ^a	Recovered 1d (%)	Decomposition products (%)
1	Benzene	Ar, 3 h, 78 °C, in light	100	
2	Cumene	Ar, 3 h, 78 °C, in light	100	
3	Cumene	Ar, 9 h, 100 °C, in the dark	92	$Ph_3COH 1g^{b}(3), Ph_2CO^{b}(2)$
4	Cumene	Ar, 156 days, room temp., in light	57	Ph ₃ CH 1c (12), Ph ₃ COEt 1e (16), Ph ₃ COH 1g ^b (7), Ph ₃ CO ^{b,c}
5	Cumene	Ar, 16 h, 153 °C, in light		Ph ₃ CH lc (75)
6	Benzene	O_2 , 15 h, room temp., in the dark	100	3
7	Benzene	O_2 , 15 h, room temp., in light	82	(Ph ₃ CO) ₂ (7), [EtOC(=S)S] ₂ 7 (6), Ph ₃ COH 1g (2), Ph ₂ CO (3)
8	Benzene	O_2 , 60 h, room temp., in light	64	(Ph ₃ CO) ₂ (15), [EtOC(=S)S] ₂ 7 (20), Ph ₃ COH 1g (6), Ph ₂ CO (7)
9	Bu'Ph	O_2 , 6 days, 80 °C, in light		Ph ₃ COEt le (22), Ph ₃ CSEt lf (10.5), Ph ₃ COH lg (22), Ph ₂ CO (40)

^a Ar: the tubes containing the solutions were flushed with and sealed under argon; O_2 : a stream of oxygen was bubbled through the reaction mixtures throughout the reactions; light means ordinary laboratory light, dark means that the tubes containing the solutions were wrapped in aluminium foil and subjected in this way to the conditions specified. ^b Probably formed as a result of traces of oxygen present in the mixture. ^c Traces detected by TLC.



Scheme 1. Reaction of triphenylmethyl halides with lithium thiolates. X = Br, Cl; $R = Pr^{i}$, Bu^{n} , Ph. Boxes denote radical-anion-radical and radical pairs, respectively.

and preparative studies, the conditions under which compound **1d** is stable.

No ESR-active species were observed in solutions of compound 1d in cumene or t-butylbenzene at room temperature in the dark. (Throughout this paper 'in the dark' means that the tubes containing the solutions were wrapped in aluminium foil.) When exposed to ordinary laboratory light or heated to ca. 90 °C in the dark both solutions exhibited the well known ESR signal ^{2c,3b} of the triphenylmethyl radical. The concentration of these radicals increased considerably when the solutions were heated to ca. 120 °C or exposed for a few minutes to sunshine. Contrary to expectation, our preparative studies (Table 1) indicated that, under argon, compound 1d is practically completely stable for reasonable periods of time at temperatures up to 78 °C in ordinary laboratory light and up to 100 °C in the dark. The same is true in the dark at room temperature in the presence of oxygen. The quantitative or practically quantitative recovery of compound 1d (entries 1-3, 6) does not mean, however, that compound 1d is indeed stable under these conditions. On the other hand, as shown by the results of experiments 4, 5 and 7-9 as well as by our ESR studies, the triphenylmethyl-to-sulphur bond of compound 1d is prone to homolysis even at room temperature. [The formation of bis-(triphenylmethyl) peroxide from O,O'-diethyl S-triphenylmethyldithiophosphate on recrystallization from benzene⁵ may be the result of an analogous homolysis and subsequent oxidation of the resulting triphenylmethyl radicals by air. Further related reactions are the homolyses of the corresponding C-S bonds of O-alkyl S-benzyl and S-acyl Oalkyl xanthates brought about by irradiation.⁶] The resulting triphenylmethyl and xanthyl radicals 6a may be expected to undergo a variety of subsequent reactions, viz. (i) recombination of two dissimilar radicals to regenerate compound 1d, (ii)

recombination of two triphenylmethyl radicals to form, in a reversible manner, the semibenzene-type α , para dimer 4 which, because of the absence of a sufficiently strong base, does not rearrange into its fully aromatic isomer 3 and is, therefore, a permanent source of triphenylmethyl radicals, (iii) recombination of two xanthyl radicals 6a to form disulphide 7 [the feasibility of this reaction is demonstrated by the formation of compound 7 by oxidation of potassium xanthate], (iv) hydrogen abstraction by triphenylmethyl radicals from cumene to afford the reduction product 1c, (v) trapping of triphenylmethyl radicals by molecular oxygen to afford triphenylmethylperoxyl radicals and thence the oxygenation products triphenylmethanol 1g and benzophenone (see ref. 1), and (vi) reaction of triphenylmethyl radicals with disulphide 7 to regenerate the *ipso* substitution product 1d, see equations (1) and (2). The feasibility of reactions (1) and (2) is demonstrated

$$Ph_{3}C' + [EtOC(=S)S]_{2} \longrightarrow$$
7
$$Ph_{3}CSC(=S)OEt + S_{2}COEt \quad (1)$$
1d
6a
$$Ph_{3}C' + 6a \longrightarrow 1d \quad (2)$$

by the observation that when equimolar mixtures of dimer 4 and disulphide 7 were kept in t-butylbenzene solution for 9 days, and in benzene solution for 18 days, at room temperature, compound 1d was indeed obtained (54 and 67% respectively) and unchanged disulphide 7 was recovered (33 and 19%, respectively.)* The unchanged dimer 4 was recovered as bis(triphenylmethyl) peroxide (34 and 21%, respectively) by oxidation of the triphenylmethyl radicals during work-up. (A further, apparently reasonable, mechanism for the formation of compound 1d, viz. homolytic dissociation of disulphide 7 and subsequent recombination of the resulting xanthyl (6a) with triphenylmethyl radicals, appears to be less probable because of our failure to detect any ESR-active species when

^{*} For similar reactions of dimer 4 with bis-[4-(dimethylamino)phenyl] and diphenyl disulphide, see refs. 7 and 8.

t-butylbenzene solutions of disulphide 7 were heated under argon at up to 162 °C in the cavity of an ESR spectrometer.)

The rate of reaction (1) appears to be considerably higher than the rates of either the homolysis of the triphenylmethyl-tosulphur bond of compound 1d or of reactions (2)–(6). Therefore, extended periods of time (entries 4 and 7–9, Table 1) or higher reaction temperatures (entries 5 and 9), preferably with the reaction mixture exposed to ordinary laboratory light, are necessary in order for detectable amounts of compounds 7, 1c, 1g and/or of benzophenone to be formed.

Furthermore, thermal rearrangement of compound 1d may be assumed to take place and to lead to the formation of S-ethyl S-triphenylmethyl dithiocarbonate 1h* and, by subsequent homolysis of the triphenylmethyl-to-sulphur bond of the latter, to triphenylmethyl radicals and the isomers **6b** of the xanthyl radical 6a. Fragmentation of radicals 6a and 6b would generate, with loss of carbon disulphide and carbonyl sulphide, ethoxy and ethylthiyl radicals, respectively. (The same fragments could also be formed by concerted homolysis of the C-S and C-O and the two C-S bonds of compounds 1d and 1h, respectively.) Recombination of the ethoxy and ethylthiyl radicals with triphenylmethyl radicals would then lead to the formation of the ether le and the sulphide lf, see Scheme 2. One or the other of the steps leading to products le and lf appears to be slow; as a result, extended reaction times are necessary for their formation in detectable amounts (entries 4 and 9).



Scheme 2. Decomposition of O-ethyl S-triphenyimethyl xanthate 1d. ^a For related rearrangements see, e.g., refs. 9 and 10. Alternatively, the two radicals could recombine to afford the isomer 8 of 1d. As discussed in connection with Scheme 3, this would be of no consequence to product composition. ^b A further possibility for the formation of the same fragments would be concerted homolysis of the C–S and C–O and the two C–S bonds of compounds 1d and 1h, respectively.

Reaction of Triphenylmethyl Bromide 1a and Potassium O-Ethyl Dithiocarbonate.—The reaction was studied under con-

ditions where O-ethyl S-triphenylmethyl dithiocarbonate 1d, its main product, had been found to be stable or where the rates of its secondary transformations could be considered as negligible in comparison with the rate of its formation. When the reaction was carried out under argon (entries 1-5, Table 2), small amounts of triphenylmethane 1c, triphenylmethanol 1g, and of the disulphide 7 as well as, in experiments 3-5, of benzophenone were obtained in addition to the main product, compound 1d. The formation of benzophenone is thought to be the result of incomplete removal of oxygen from the system. Triphenylmethanol 1g, too, is an oxygenation product; a further mode of its formation, which does not involve participation of oxygen, is hydrolysis of unchanged starting bromide 1a during work-up. The triphenylmethanol obtained in experiment 1 and part of it obtained in experiments 3–5 appears to be formed by the latter process. Formation of the two oxygenation products as well as of disulphide 7 was, of course, also noticed when the title reaction was carried out under oxygen (entries 6-8). The yield of these products increased when the reaction was run in ordinary laboratory light rather than in the dark (compare entries 6 and 7) as well as when extended reaction times were applied (compare entries 7 and 8).

The formation of triphenylmethane 1c, the disulphide 7, and of the oxygenation products (which had been shown¹ to be formed, in related cases, via triphenylmethylperoxyl radicals, the trapping products of triphenylmethyl radicals by molecular oxygen) appears to indicate that triphenylmethyl and xanthyl radicals 6a were present as intermediates in our reaction mixtures. Support for this view came from ESR studies. Mixtures of bromide 1a, potassium xanthate and benzene or cumene, sealed under argon, were found to exhibit, even at room temperature, the ESR spectrum of triphenylmethyl radicals, their concentration increasing with increasing temperature as well as on irradiation with visible light. Triphenylmethyl radicals were detected in mixtures of bromide 1a, potassium xanthate and cumene also in air; when these mixtures were vigorously shaken, the intensity of the triphenylmethyl radical signal rapidly diminished, obviously as a result of trapping of the radicals by molecular oxygen. Three further observations are of importance in the present connection, viz. that (i) O-ethyl S-triphenylmethyl dithiocarbonate 1d is quantitatively recovered after heating of its solutions in benzene or cumene for 3 h at 78 °C under argon in the dark or by exposing it in benzene solution at room temperature to ordinary laboratory light for 15 h under oxygen (entries 1, 2 and 6, Table 1), (ii) in the absence of potassium Oethyl dithiocarbonate but otherwise under the conditions of experiment 6 of Table 2 bromide 1a practically does not react: when the resulting mixture was poured into ethanolic sodium ethoxide, 95% of the ether 1e and 3% of triphenylmethanol 1g, the products of ethanolysis and hydrolysis, respectively, of unchanged bromide were recovered, and (iii) when heated in the absence of potassium O-ethyl dithiocarbonate for 9 h at 100 °C in cumene under argon (cf. experiment 3, Table 2), bromide 1a gave, after hydrolytic work-up, triphenylmethanol 1g (96%), resulting from unchanged bromide 1a, along with triphenylmethane lc (1%). Together with these observations the results of experiments 1, 2 and 4-6 of Table 2 appear to indicate that the formation of triphenylmethyl and xanthyl radicals 6a is the result of SET from O-ethyl dithiocarbonate anions to bromide 1a, rather than of the secondary homolysis of initially formed dithiocarbonate 1d; in other words, in addition to polar mechanisms, participation of SET-initiated radical mechanisms in the formation of the *ipso* substitution product 1d should be taken into consideration. (The amount of dithiocarbonate 1d isolated in experiments 3, 7 and 8, Table 2, does not differ much from the amount of recovered starting material after treatment of compound 1d under comparable conditions; see entries 3, 7 and 8, respectively, of Table 1. Therefore, in experiments 3, 7 and 8,

^{*} For related rearrangements see, e.g., refs. 9 and 10.

			Products and yields (%)							
	Solvent	Conditions ^b	Ph ₃ CSC(=S)OEt 1d	Ph ₃ CH 1c	[EtOC(=S)S] ₂ 7	Ph ₃ COH 1g	Ph ₂ CO	(Ph ₃ CO) ₂		
1	Benzene	Ar, 6 h, room temp., in the dark	94		2	2°				
2	Benzene	Ar, 6 h, 60 °C, in the dark	84		-	_				
3 ^d	Cumene	Ar, 9 h, 100 °C, in the dark	88	1	2	4 ^e	35			
4	Benzene	Ar, 6 h, room temp., in light	86		1	7 e	15			
5	Benzene	Ar, 6 h, room temp., in light ⁹	79		2	4 ^e	25			
6 ^h	Benzene	O_2 , 6 h, room temp., in the dark	81		4	4	3			
7	Benzene	O_2 , 6 h, room temp., in light	81		7	8	4			
8	Benzene	O_2 , 52 h, room temp., in light	48		24	18	12	16		

Table 2. Reaction of triphenylmethyl bromid	1a with potassium O-ethyl dithiocarbonate. ^a
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^a Equimolar amounts of the starting compounds were vigorously stirred in benzene or in the hydrogen-atom donor cumene $(10 \text{ cm}^3/\text{g} \text{ bromide } 1a)$ under the conditions specified. ^b Ar: the tubes containing the reaction mixtures were flushed with and sealed under argon; O₂: a stream of oxygen was bubbled through the reaction mixtures throughout the reactions; light means ordinary laboratory light, dark means that the tubes containing the reaction mixtures were wrapped in aluminium foil and subjected in this way to the conditions specified. ^c Formed by hydrolysis of unchanged bromide during work-up. ^d Heating of bromide 1a in the dark under Ar for 9 h at 100 °C in cumene in the absence of potassium *O*-ethyl dithiocarbonate furnished, after hydrolytic work-up of the reaction mixture, triphenylmethanol 1g (96%), resulting from unchanged bromide, and triphenylmethane 1c (1%). ^e Formed partly by hydrolysis of unchanged bromide during work-up and partly as a result of incomplete removal of oxygen from the reaction mixture. ^f Probably formed as a result of incomplete removal of oxygen from the reaction mixture. ^e 1 mmol of *m*-DNB for each mmol of bromide 1a was added; 93% of the nitro compound was recovered unchanged. ^b When bromide 1a was heated under the same conditions, except for the absence of potassium *O*-ethyl dithiocarbonate, and the reaction mixture was poured into ethanolic sodium ethoxide, the starting bromide was recovered in the form of the ether 1e (95%) and triphenylmethanol 1g (3%), its ethanolysis and hydrolysis product, respectively.



Scheme 3. Conceivable mechanisms of formation of the *ipso* substitution product 1d. Boxes denote radical-anion-radical and radical pairs, respectively. Mechanism 1: Direct polar substitution $(S_N 2)$, equation (3). Mechanism 2: Sequence of two polar reactions, equations (4) and (5). Mechanism 3: SET-initiated non-chain process, equations (7) + (8). Mechanism 4: SET-initiated chain process $(S_{RN} 1)$, equations (7) + (9) + (10).

Table 2, formation of part of the triphenylmethyl and xanthyl radicals **6a** by secondary homolysis of initially formed dithiocarbonate **1d** may not be ruled out.)

A priori at least four reasonable mechanisms may be formulated for the formation of compound 1d: two polar and two SET-initiated mechanisms (Scheme 3). The simplest mechanism would be direct nucleophilic attack of xanthate anions at the central carbon atom of bromide 1a or the corresponding ion pair which is essentially an S_N^2 reaction [equation (3)]. Because of the bulky ligands attached to the central carbon atom of bromide **1a** this reaction should be subject to severe steric hindrance. Therefore, alternative attack of xanthate anions at one of the *para* carbon atoms of the bromide does not appear unlikely; this would lead, in what is essentially an S_N2' reaction, to the formation of a semibenzene-type intermediate **8** [equation (4)]. Attack of a second xanthate anion at the central carbon atom of bromide **1a**, is planar-

trigonal and therefore considerably less shielded against nucleophilic attack) could then lead, with loss of the xanthate group introduced during the previous step, in a second S_N2'type reaction [equation (5)] to the ipso product. [For analogous reactions of triphenylmethyl halides and related compounds with anionic O-nucleophiles, see refs. 2(d) and 11.] An expected additional mode of stabilization of semibenzene 8 would be rearomatization by base-catalysed deprotonation and subsequent protonation to give the tele substitution product 2b [equation (6)]; however, compound 2b was not present among the reaction products [although analogous tele substitution products 2a were obtained in the related studies of Ashby et al.³]. The non-formation of compound 2b does not necessarily rule out the operation of equations (4) + (5): an alternative explanation of its non-formation could be that the only base present in our reaction mixtures is the xanthate anion whose nucleophilicity towards carbon considerably surpasses its basicity; as a result, reaction (6) is completely suppressed.

A further possible mode of reaction of bromide 1a and xanthate anions is SET from the latter to the former which would lead, either via the intermediacy of the radical anions 9 or directly by dissociative ET, to the formation of triphenylmethyl radicals [equation (7)]. Recombination of the latter with xanthyl radicals 6a [equation (8)] either in the solvent cage or after their escape from the cage by chance encounters would constitute the final step of an SET-initiated non-chain process leading to the *ipso* substitution product 1d. [An alternative mode of recombination of the same radicals could lead to semibenzene 8. Since the latter is, under the present conditions, incapable of rearranging according to reaction (6) but may be expected to undergo homolysis easily and thereby regenerate the radicals from which it was formed, its formation would be of no consequence to the product composition.] The triphenylmethyl radicals could, furthermore, after their escape from the solvent cage, react with xanthate anions to give intermediate 10 [reaction (9)] which, together with reaction (10), would constitute the propagation cycle of an SET-initiated reaction (an S_{RN} reaction ^{12,13}) leading to the *ipso* substitution product 1d.

In order to gain further support for the contribution of SETinitiated radical reactions to the formation of the ipso substitution product 1d, the effect of added m-dinitrobenzene (m-DNB) on the reaction was studied and trapping experiments were carried out. Addition of m-DNB (1 mol equiv.) to the reaction mixture had no appreciable effect on the yield of compound 1d (entries 4 and 5, Table 2) and unchanged m-DNB was recovered almost quantitatively. m-DNB is a well known radical-anion scavenger (electron trap); therefore, its negligible effect on the yield of compound 1d appears to militate strongly against the operation of an S_{RN}1 mechanism. [According to the literature, 3b,12 p-DNB is usually preferred to m-DNB as an electron trap. We have, however, noticed that in some cases rapid substitution of one of the nitro groups of p-DNB by the nucleophile may take place. As a result, and depending on the molar ratio of the nucleophile and p-DNB, either the former is rapidly consumed (its reaction with the halide both via polar and SET-initiated mechanisms being thereby prevented) or the latter is converted into mono-nitro derivatives of the type 4-NuC₆H₄NO₂ which are less active electron acceptors than p-DNB. With m-DNB we have not noticed similar complications so far.] Ashby et al. noticed the negligible effect of added p-DNB on the reaction of bromide 1a with lithium propane-2-thiolate. From this and the negligible effect of added DCPH on the rates of reaction of bromide **1a** with lithium thiolates they similarly concluded that operation of the $S_{RN}1$ mechanism in these cases is unlikely.³¹

Dicyclohexylphosphine (DCPH) which, due to its weak P-H bond, is extensively used as a hydrogen-atom donor and radical

trap,^{3b,14} and molecular oxygen were considered for use as trapping agents. However, our recent observations, according to which both tributyl- and triphenyl-phosphine are able to generate triphenylmethyl radicals from triphenylmethyl halides,¹ indicated that the same reaction could be brought about by DCPH. Therefore, if at all, DCPH should be used only with caution as a probe for the intermediacy of triphenylmethyl radicals generated from triphenylmethyl halides. Indeed, when benzene solutions of triphenylmethyl bromide 1a and DCPH (molar ratio 1:4.6) were sealed under argon and kept for 65 h at room temperature or for 6 h at 60 °C, in both cases in the dark, the reduction product triphenylmethane 1c (87 and 94%, respectively) was isolated. This obviously means that DCPH exerts a double role: it indeed acts as a single-electron donor to generate, similarly to the tertiary phosphines mentioned above, triphenylmethyl radicals which are immediately trapped either by a second molecule of DCPH [equation (11)] or by the radical cation of DCPH, to yield the hydrogen-transfer product 1c [equations (12), (13); $R = c \cdot C_6 H_{11}$]. [Although the P-H bond of R₂PH (DCPH) is considerably weaker than its C-H bonds, the relative strengths of the P-H and the α-C-H bonds of the corresponding radical cation appear not to be known. Therefore it is uncertain whether triphenylmethyl radicals and the radical cations of DCPH react according to equation (12) or equation (13).]

$$Ph_{3}C \bullet + R_{2}PH \longrightarrow Ph_{3}CH + R_{2}P \bullet$$
(11)
1e

$$Ph_{3}C + O PHR + O$$

As a consequence, even if addition of DCPH to mixtures of triphenylmethyl bromide 1a, potassium O-ethyl dithiocarbonate and benzene or similar solvents resulted in an increase in the relative yield of the reduction product 1c (as it indeed does), this would not prove that potassium O-ethyl dithiocarbonate does act as a single-electron donor in the reaction because it would remain unclear whether the triphenylmethyl radicals, the precursors of the reduction product, are formed as a result of SET to bromide 1a from the dithiocarbonate or from DCPH.

The comparatively low yields of both triphenylmethane 1c and the oxygenation products triphenylmethanol 1g and benzophenone may be understood by assuming either that, under the conditions applied in the present study, the *ipso* product is mainly formed by the polar mechanism [mechanism (2), Scheme 3] or, if the S_{ET} pathway were the main route leading to compound 1d, that the rate of recombination of triphenylmethyl and xanthyl radicals 6a is considerably greater than the rates of both the hydrogen abstraction from cumene by triphenylmethyl radicals and trapping of the latter by molecular oxygen. Since at least part of the recombination of triphenylmethyl and xanthyl radicals is an in-cage process, this assumption appears to be reasonable.

If mechanisms (2) and (3) of Scheme 3 were indeed competing routes leading to the same product 1d, elevation of the reaction temperature should favour the SET-initiated mechanism (3).¹⁵ Owing to the fact that, at elevated temperatures, homolysis of the triphenylmethyl-to-sulphur bond of compound 1d becomes prominent, a study of the title reaction at elevated temperatures was considered to be to no avail because it would remain uncertain whether the isolated products are primary products or secondary decomposition products of the originally formed *ipso* product 1d.

Experimental

M.p.s are not corrected and were determined in glass capillaries. Purification of the various products was carried out by column chromatography (Kieselgel 60, 230–400 mesh ASTM, E. Merck, Darmstadt, Art. 9385) or preparative TLC (PLC) (20×20 cm plates, coated with Kieselgel PF₂₅₄₊₃₆₆). Most of the products described in the present paper were known compounds and were identified by m.p. and mixed m.p. determinations, and by comparison of their IR and $R_{\rm f}$ -values with those of authentic samples. ¹H NMR spectra were recorded, unless otherwise stated, with a Perkin-Elmer R-12 spectrometer at 60 MHz for CDCl₃ solutions with Me₄Si as the internal reference. A JEOL JES-FE/3X spectrometer (100 kHz, field 3233 ± 50 G, mod. 0.26 G) was used for the ESR studies.

Starting Substances and Solvents.—Triphenylmethyl bromide 1a (Merck, Darmstadt), contaminated by traces of benzophenone, was purified by recrystallization from acetic acidacetic anhydride-phosphorus tribromide [9:1:0.2 (v/v)]. Potassium xanthate was obtained as described in the literature.¹⁶ Dicyclohexylphosphine (DCPH) was obtained via dicyclohexylphosphinic acid and dicyclohexylphosphinoyl chloride essentially as described in the literature.¹⁷ The product was stored in sealed glass ampoules under argon. The solvents benzene, cumene and t-butylbenzene were purified by distillation at normal pressure and stored over sodium wire.

Since the methods described in the literature¹⁸ for the preparation of dimer 4 furnished, in our hands, products contaminated with some triphenylmethyl chloride or triphenylmethanol, the following procedure for the preparation of the dimer was developed. A vigorously stirred mixture of mercury (50 g, 250 mmol), bromide 1a (18.4 g, 57 mmol) and dry benzene (150 cm^3) was refluxed for 3 h in a stream of argon in the dark. The mixture was allowed to cool and the insoluble inorganic material to settle. The supernatant was transferred under argon into another flask and evaporated to dryness under reduced pressure.

Anhydrous acetone was added to the warm residue and the resulting solution was gradually cooled, and finally kept for 2 h in an ice-salt-bath. The crystalline crude product was recrystallized twice from acetone, all operations being carried out under argon. The product was identified by its m.p. (152-154 °C; lit.,^{18a} 152-153 °C), its ready solubility in benzene, the fading of the orange colour of this solution, and the quantitative conversion of the product into bis(triphenylmethyl) peroxide, m.p. 186 °C (from 1,2-dichloroethane) (lit.,¹⁹ 185-186 °C), when the solution was shaken for a sufficient period or allowed to evaporate to dryness in air. According to TLC (benzene) the product was slightly contaminated by bis(triphenylmethyl) peroxide lut did not contain even traces of the starting bromide 1a or triphenylmethanol 1g.

Ethyl triphenylmethyl sulphide 1f, m.p. 129–130 °C (from EtOH) (lit.,²⁰ 132–133 °C;²¹ 125 °C) was obtained as described in the literature;²¹ δ_{H} (200 MHz; Varian FT) 1.05t + 2.14q (J 7 Hz, SEt) and 7.1–7.5 (m, 15 × ArH).

O,O'-Diethyl Dithiobis(thiocarboxylate) 7.—A mixture of potassium xanthate ¹⁶ (16 g, 0.1 mol), iodine (12.1 g, 95 mmol) and water (80 cm³) was stirred for 2 h at 14 °C to give a crystalline precipitate (8.8 g) of the title compound which, according to TLC (hexane), was almost pure. Recrystallization from methanol gave compound 7 as crystals, m.p. 32–33 °C (lit.,²² 32–32.5 °C), which were collected after the mixture had been kept for 1 day at 0–5 °C and for 2 days at -20 °C; $\delta_{H}(200 \text{ MHz}; \text{Varian FT})$ 1.45t + 4.7q (J7 Hz; intensity ratio 3:2; OEt).

Decomposition of O-Ethyl S-Triphenylmethyl Dithiocarbonate 1d in Aromatic Hydrocarbons under Various Conditions (Table

1).--(a) Under argon (entries 1-5). Solutions of compound 1d (0.45-1.3 g, 1.25-3.6 mmol) in benzene or cumene $(5-10 \text{ cm}^3)$ were placed in thick-wall glass tubes, flushed with and sealed under argon, and subjected to the conditions specified in Table 1. The resulting solutions were examined by TLC and evaporated to dryness. If a single substance was shown to be present, the residue was recrystallized from propan-2-ol (experiments 1 and 2) and ethanol (experiment 5), respectively. If mixtures of products were obtained, they were worked up either by column chromatography [experiment 3; hexane ----- benzene-hexane (1:1)] or by PLC [experiment 4; development: EtOAc-hexane (2:18); elution: CH_2Cl_2 -methanol (1:1); rechromatography of the non-homogeneous fractions, development: benzene-hexane (1:1); elution as above] to give the products listed in Table 1. All products were identified by comparison (m.p., IR, TLC) with authentic samples.

(b) Under oxygen (entries 6-9). Solutions of compound 1d (0.45-1.3 g, 1.25-3.6 mmol) in benzene or t-butylbenzene (5-10 cm³) were placed in small, round-bottom flasks and subjected to the conditions specified in Table 1 with introduction of a continuous stream of oxygen into the mixtures throughout the reaction. The mixtures were evaporated to dryness at reduced pressure. In experiment 6 the residue was shaken with a mixture of CH_2Cl_2 and water (60 cm³, each); the organic phase was dried (MgSO₄) and evaporated to dryness. The residue was shown by TLC, IR and ¹H NMR spectroscopy to contain a single substance, viz. the unchanged starting compound. In experiments 7 and 8 the residues were triturated with diethyl ether (40 cm³) to precipitate crystals of bis(triphenylmethyl) peroxide. The mixtures were kept for ca. 4 h in a refrigerator and the peroxide was filtered off and washed with a small amount of diethyl ether. The combined filtrate and washings were evaporated to dryness and worked up by column chromatography (benzene-hexane mixtures containing gradually increasing amounts of benzene) to afford the products listed in Table 1.

Reaction of Dimer 4 with Disulphide 7.—The dimer 4 (0.87 g, 1.8 mmol) and the disulphide 7 (0.43 g, 1.8 mmol) were allowed to react (a) in t-butylbenzene (10 cm³) for 9 and (b) in benzene (10 cm³) for 18 days at room temperature in argon-flushed sealed tubes and the reaction mixtures were worked up by column chromatography [hexane \longrightarrow benzene-hexane (1:3)] to give unchanged disulphide 7 (a: 0.14 g, 33%; b: 0.08 g, 19% recovery), O-ethyl S-triphenylmethyl dithiocarbonate 1d (a: 0.7 g, 54%; b: 0.87 g, 67%), and bis(triphenylmethyl) peroxide (a: 0.31 g, 34%; b: 0.19 g, 21%), the latter being formed by oxidation of unchanged dimer 4 during work-up.

Reaction of Triphenylmethyl Bromide 1a with Potassium Xanthate (Table 2).—(a) Under argon (experiments 1–5). Equimolar mixtures of triphenylmethyl bromide 1a and potassium xanthate (3.6 mmol, each), benzene or cumene (10 cm^3) (which had been refluxed for ca 20 h over potassium and sodium metal, respectively, and distilled under argon) as well as, in experiment 5, an equimolar amount of the radical-anion scavenger m-DNB and, because of the poor solubility of the xanthate, a small, Teflon-coated magnetic stirrer bar were placed in thick-wall glass tubes and flushed with argon as described in ref. 23 for the reaction of triphenylmethyl chloride with tributylamine in cumene. The tubes were sealed under argon and the reactions were conducted under the conditions specified in Table 2 but otherwise as described in ref. 23. The mixtures were allowed to cool, diluted with benzene or CH_2Cl_2 (ca. 50 cm³), washed with water (ca. 50 cm³), dried (MgSO₄) and evaporated to dryness. The residue obtained in experiment 2 proved homogeneous (TLC) and was therefore directly crystallized from propan-2-ol. The residues resulting from experiments 1 and 3-5 were worked up by column chromatography [hexane ----- benzene--hexane $(1:10) \longrightarrow (1:3) \longrightarrow (1:1)$]. Individual fractions were identified by comparison (m.p., TLC, IR and, if necessary, ¹H NMR spectroscopy) with authentic samples.

During work-up of the residue obtained in experiment 3 it was noticed that compounds 1c and 7 could not be separated by chromatography in the systems used. The relative amounts of these two compounds were determined either on the basis of the ¹H NMR spectrum of their mixture or by comparison of the IR spectrum of their mixture with those of mixtures of known compositions, or by refluxing weighted amounts of the mixture for 10 min with ethanolic potassium hydroxide, evaporation to dryness, and isolation of the unchanged triphenylmethane 1c by taking up the residue in water-diethyl ether and work-up of the ethereal solutions in the usual manner. The results obtained by the chemical and the spectroscopic methods were consistent.

O-Ethyl *S*-triphenylmethyl dithiocarbonate **1d**, m.p. 142– 143 °C (from PrⁱOH) [lit.,²⁴ 139 °C (from EtOH–Et₂O)] (Found: C, 72.55; H, 5.9; S, 17.6. Calc. for $C_{22}H_{20}OS_2$: C, 72.48; H, 5.53; S, 17.59%); δ_H 0.77t + 4.19q (*J* 7 Hz, OEt) and 7.21s (3 × Ph).

(b) Under oxygen (experiments 6-8). Equimolar mixtures of triphenylmethyl bromide 1a, and potassium O-ethyl dithiocarbonate (3.6 mmol, each) in benzene (10 cm³), pretreated as described in (a), were allowed to react in a continuous stream of dry oxygen under the conditions specified in Table 2, and worked up by column chromatography as described in (a) to yield the products listed in Table 2.

Control Experiments: Reaction of Bromide 1a with Aromatic Hydrocarbons under Various Conditions.—(a) A mixture of bromide 1a (3.6 mmol) and cumene (10 cm³) (pretreated as described above) was subjected to the conditions of experiment 3, Table 2, and allowed to cool. Water was added and the vigorously stirred mixture was refluxed for 20 min. The organic layer was dried (MgSO₄), evaporated to dryness and worked up by column chromatography [hexane — benzene-hexane (1:10) — (1:3) — (1:1)] to give triphenylmethanol 1g (96%) and triphenylmethane 1c (1%), identified by comparison (TLC, IR) with authentic samples.

(b) A mixture of bromide **1a** (3.6 mmol) and benzene (10 cm³) (pretreated as described above) was subjected to the conditions of experiment 6, Table 2, and evaporated to dryness. An ethanolic (15 cm³) solution of metallic sodium (0.18 g, 7.8 mmol) was added, and the mixture was refluxed for 5 min and evaporated to dryness. The residue was vigorously shaken with CH₂Cl₂ (50 cm³) and water (30 cm³), and the organic layer was dried (MgSO₄), evaporated to dryness, and worked up by column chromatography as in (a) to give the ether **1e** (95%) and triphenylmethanol **1g** (3%), identified by comparison (TLC, IR) with authentic samples.

Reduction of Bromide 1a by Dicyclohexylphosphine (DCPH). —(a) A mixture of bromide 1a (1.16 g, 3.6 mmol), DCPH¹⁷ (3.26 g, 16.5 mmol) and benzene (10 cm³) (pretreated by refluxing over molten potassium metal and distillation under Ar) was placed, together with a small, Teflon-coated magnetic stirrer bar, into a thick-wall glass tube. The tube was wrapped in aluminium foil, flushed with and sealed under argon, and the mixture was stirred for 65 h at ambient temperature. The solvent was distilled off under reduced pressure in the dark (bath temperature 25 °C) and the residue was worked up by column chromatography [hexane \longrightarrow toluene-hexane (1:15)] to give of triphenylmethane 1c (0.76 g, 87%) which proved identical (m.p., 1R, TLC) with an authentic sample. (b) When the same experiment was carried out at 60 $^{\circ}$ C (6 h), compound 1c (0.82 g, 94%) was obtained.

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